

ACALYPHA FRUTICOSA AS CORROSION INHIBITOR FOR MILD STEEL IN ACID MEDIUM

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ABSTRACT

The inhibition efficiency of the extract of *Acalypha fruticosa* for the corrosion of mild steel in 1N H₂SO₄ was investigated by weight loss, Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and Scanning Electron Microscope (SEM) techniques. The results indicate that leaves of AF serve as a good corrosion inhibitor of mixed type with efficiency as high as 97.92 % at 0.3% inhibitor concentration.

KEYWORDS: Acalypha Fruticosa, Mild Steel, Acid Medium, Corrosion Inhibitor

INTRODUCTION

Corroion is the disintegration of an engineering material into its constituent atom due to chemical reaction with its surroundings or electrochemical oxidation of metal in reaction with an oxidant such as oxygen ^[1]. Several industries use acid solutions for cleaning, descaling and pickling of steel structure. These processes are normally accompanied by considerable dissolution of the metal. Corrosion inhibitors are used to reduce the loss due to metal dissolution. Compounds containing hetero atoms like N, S, O and inorganic compounds like chromates, Phosphates, molybdates etc., are being investigated as corrosion inhibitors ^[2-7]. Most of the synthetic compounds are toxic and cause severe environmental hazards, use of plant extract as eco-friendly, non-toxic & harmless corrosion inhibitor is of significance ^[8-15].

In the present work, an attempt was made to find a naturally occurring, cheap & environmentally safe substance that can be employed for inhibiting the corrosion of mild steel in acidic medium. In this present work, leaves of *Acalypha fruticosa* (AF), as corrosion inhibitor for mild steel in 1N Sulphuric acid by weight loss. Polarization, impedacce and SEM techniques.

EXPERIMENTAL

Material Preparation

Rectangular samples of area 5 cm² have been cut from a large sheet of mild steel. The samples were polished, drilled a hole of one end and numbered by punching. During the study, the samples were polished with four grade emery papers, degreased in solution of non-toxic detergent then with acetone finally washed with distilled water and stored in desiccators. Accurate weights of the samples were taken using electronic balance. The exposed area for polarization studies of the mild steel specimen was 1cm².

Inhibitor Preparation

The leaves of *Acalypha fruticosa* were powdered well. The extract was prepared by refluxing 15 gm of *Acalypha fruticosa* powder in 500 ml of 1N H₂SO₄ for three hours. It was kept overnight and the solution was filtered. The residue was repeatedly washed with small quantities of 1N H₂SO₄ and the filtrate was made up to 500ml. From the stock solution different concentrations of the extract from 0.003%, 0.015%, 0.09%, 0.3% v/v were prepared.

Weight Loss Method

The initial weights of the polished plate were noted. The sample was immersed using glass hooks in triplicate in 1N H₂SO₄ solution contained in a 100 ml beaker, both in absence and presence of inhibitor for different intervals of time (Table 1). The specimens were taken out, washed with deionized water, dried and reweighed. The inhibition efficiency (IE%) was calculated using the formula (1).

Temperature Study

Weight loss determinations were carried out at different temperatures (303K, 313K, 323K, and 333K). After initial weighing, the specimens were immersed in 100ml of blank 1N H₂SO₄ and in 1N H₂SO₄ containing different concentrations (0.015%, 0.09%, 0.3% v/v) of the plant extract at the above temperatures. The thermostat was set at the appropriate temperature and after 1hr immersion the specimens were removed, washed, dried, and reweighed.

Calculation of Corrosion Parameters

- Inhibitor Efficiency was calculated using the formula

$$\text{Inhibitor Efficiency(\%)} = \frac{\left\{ \begin{array}{c} \text{weight loss} \\ \text{without inhibitor} \end{array} \right\} - \left\{ \begin{array}{c} \text{weight loss} \\ \text{with inhibitor} \end{array} \right\}}{\text{weight loss without inhibitor}} \times 100$$

- Corrosion rate (CR)

The corrosion rate was determined using the formula

$$\text{Corrosion rate} = \frac{534 \times W}{DAT}$$

mpy - Mils per year.

W - Weight Loss in Milligrams.

D - Density in g/cm². (7.9 g/cm² for mild steel)

A - Area of Specimen in Square Inches.

T - Exposure Time in Hours.

Electrochemical Studies

Electrochemical measurements were carried out using the conventional three electrode cell with a platinum electrode as the counter electrode, a saturated calomel electrode as reference electrode and the mild steel electrode as working electrode in a 100ml glass beaker.

The polarization measurements were carried out from a potential range of -200mV to $+200\text{mV}$ with respect to open circuit potential in presence and absence of inhibitor at a scan rate of 1mV/sec . The log of current and the corresponding potentials were fed into the plotter and a potential E vs $\log I$ plot was obtained. The corrosion current I_{corr} was obtained from the Tafel plot by extrapolation of the linear portion of the curve to E_{corr} and the slope of the linear region were the Tafel slopes b_a and b_c which were calculated using 'Powersuite' software.

The electrochemical impedance measurements were carried out for mild steel in acid media using electrochemical measurement unit (Parstat 2273). The impedance measurements were made at corrosion potentials over a frequency range of 0.1 to 20000 Hz with signal amplitude of 10mV . The results are presented in the form of Nyquist plot. From the plot, the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were calculated using the 'Zsimpwin' software.

SEM Studies

The surface studies of the specimen after immersion for 1 hr at 30°C in $1\text{N H}_2\text{SO}_4$ and $1\text{N H}_2\text{SO}_4$ containing inhibitor was performed on a model JSM – 6390 scanning electronic microscope.

RESULTS AND DISCUSSIONS

The IE of the plant extract in $1\text{N H}_2\text{SO}_4$ as calculated by gravimetric method with different inhibitor concentrations and different immersion periods is indicated in Table I. The IE was found to increase from 75.0% at inhibitor concentration of 0.003% v/v up to 91.67% at inhibitor concentration of 0.3% for 1 hr immersion (fig – 1&2). Above 0.3% v/v inhibitor concentration there was not much change in efficiency. Corrosion rate is found to decrease with increase with concentration and with increased immersion time in acid. The corrosion inhibition may be due to adsorption of the phytoconstituents on the surface making a barrier for mass and charge transfers and thus preventing the metal surface from corrosion. The degree of protection increases with increasing surface coverage by the adsorbed molecules.

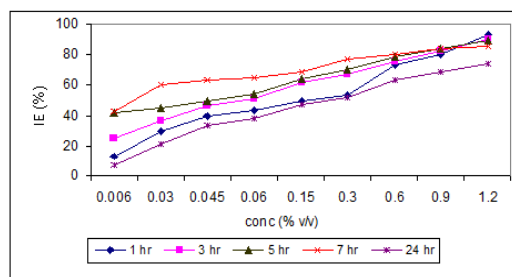


Figure1: Variation of IE (%) with Concentration of AF Leaf Extract in $1\text{N H}_2\text{SO}_4$

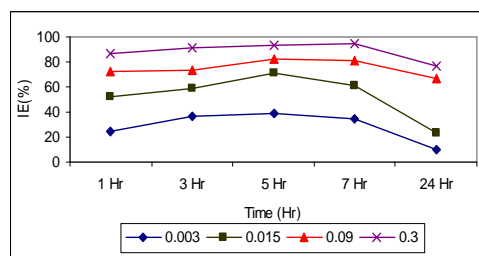


Figure2: Effect of Immersion Time on IE (%) in $1\text{N H}_2\text{SO}_4$
Without and with AF Leaf Extract

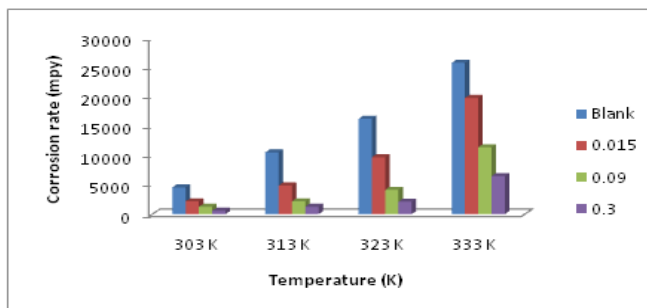


Figure 3: Variation of Corrosion Rate with Temperature at Different Concentrations of AF Leaf Extract in 1N H₂SO₄

Table 1 CR and IE (%) of AF Flower Extract in 1N H₂SO₄ at Different Concentrations and Different Immersion Periods.

S. No.	Inhibitor Conc. (% v/v)	1 hr		3 hr		5 hr		7hr		24hr	
		CR mpy	IE%	CR mpy	IE%	CR mpy	IE%	CR mpy	IE%	CR mpy	IE%
1	Blank	5069.62	-	6759.49	-	5272.405	-	4779.928	-	4787.975	-
2	0.003	1267.41	75.00	1830.70	75.42	2754.494	47.75	2583.092	45.96	3108.663	35.07
3	0.015	760.44	85.00	647.78	90.42	1216.709	76.92	1146.700	76.01	1408.228	70.58
4	0.09	506.96	90.00	366.14	94.58	371.772	92.94	350.045	92.67	429.509	91.02
5	0.3	422.47	91.67	140.82	97.92	219.684	95.83	217.269	95.45	306.290	93.60

Table 2: CR of Mild Steel and IE (%) of AF Leaf Extract on Corrosion of Mild Steel in 1N H₂SO₄ at Different Concentrations and Different Temperatures

S. No	Inhibitor Conc. (% v/v)	303 K		313 K		323K		333K	
		CR mpy	IE %	CR mpy	IE %	CR mpy	IE %	CR mpy	IE %
1.	Blank	4562.66	-	10561.71	-	16307.28	-	25855.06	-
2.	0.015	2196.84	51.85	4900.63	53.60	9716.77	40.41	19856.01	23.20
3.	0.09	1267.41	72.22	2196.84	79.20	4140.19	74.61	11406.65	55.88
4.	0.3	591.46	87.04	1267.41	88.00	2112.34	87.05	6506.01	74.84

Table 3: Thermodynamic Parameters for the Adsorption of AF Leaf Extract on Mild Steel in 1N H₂SO₄

S. No.	Inhibitor Conc. (% V/V)	-ΔG _{ads} Kj/Mol				- Δh _{ads} Kj/Mol	ΔS _{ads} Kj/Mol
		303K	313K	323K	333K		
1.	0.015	20.86	21.73	21.00	19.41	22.020	0.508
2.	0.09	18.57	20.73	20.12	18.42	19.725	0.106
3.	0.3	17.93	18.75	19.11	17.45	18.580	0.108

Table 4: Tafel Polarization Parameters for Mild Steel in 1N H₂SO₄ in Absence and Presence of AF Leaf Extract

S. No	Inhibitor conc. (% v/v)	-E _{corr} mV	I _{corr} mA cm ⁻²	β _c mV/dec	β _a mV/dec	CR mpy	R _p Ω	IE (%)	
								I _{corr}	R _p
1.	Blank	462.40	1.605 × 10 ⁻³	263.048	100.354	5.884 × 10 ³	2.533	-	-
2.	0.015	447.396	1.107 × 10 ⁻³	215.808	75.517	4.057 × 10 ³	3.304	31.02	23.33
3.	0.3	450.927	5.186 × 10 ⁻²	173.375	47.285	1.901 × 10 ³	3.670	67.68	30.98

Effect of Temperature

The results of temperature studies on CR are given in Table – 2. The corrosion rate in general increases with temperature (fig – 3). This may be due to the fact that increase in temperature accelerates corrosive process. It is found that the corrosion rate decreased considerably with increase in concentration of inhibitor for all temperatures studied showing that inhibition of corrosion takes place by adsorption process. At higher inhibitor concentration range, the inhibitor efficiency is almost the same for all temperatures indicating that it could be safely used upto 333K.

Electrochemical Experiments:

The values of E_{corr} , I_{corr} , cathodic tafel slope b_c , anodic tafel slope b_a , linear polarization resistance R_p and IE (%) based on tafel fit are given in Table 4. From the table it is noticed that E_{corr} values are centered around 500 mV and do not show much variation. This shows that the plant extracts act through mixed mode of inhibiting both anodic and cathodic reaction. I_{corr} values show steady decrease from blank acid to inhibited acid with increasing concentration of inhibitor which means that CR decreases with inhibitor concentration. The lower I_{corr} values without causing any significant changes in the corrosion potential E_{corr} suggests that the inhibitor is a mixed type one and retards both the rates of hydrogen reduction and anodic dissolution of mild steel. The values b_a and b_b have not been shifted significantly to any particular direction from the blank values indicating again the mixed mode type of inhibition. The same trend was observed for weight loss method confirming that the inhibitor mechanism involves adsorption of the extract constituents on the metal surface.

Figure 4 shows the potentiodynamic polarization curve for mild steel in 1N H_2SO_4 in the absence and presence of different concentrations of the plant extract. Both anodic and cathodic reactions are inhibited as seen from the shape of the polarization curve.

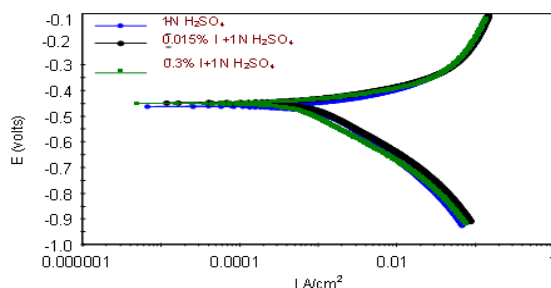


Figure 4: Potentiodynamic Polarization Plot for Mild Steel in 1N H_2SO_4 with AF Leaf Extract

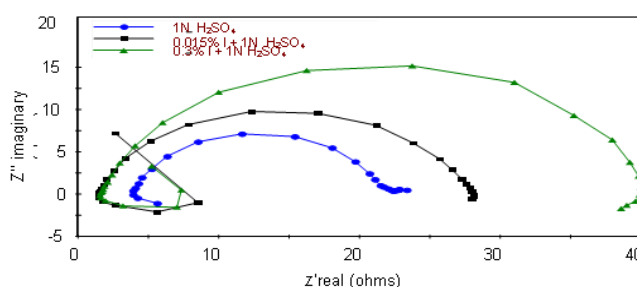
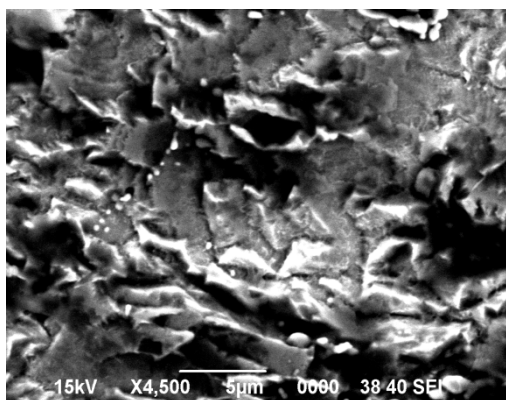


Figure 5: Nyquist Plot – Mild Steel in 1N H_2SO_4 in Absence and Presence of AF Extract

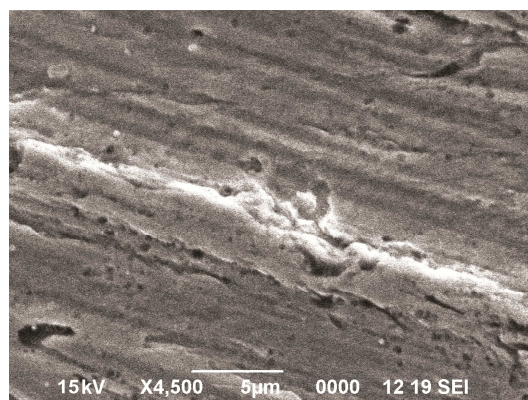
The results indicate that the double layer capacitance C_{dl} values are less for inhibitor system compared to those of uninhibited system and R_{ct} values are higher for inhibited systems. These observation indicate that the plant extract inhibit corrosion by getting adsorbed on the metal surface which increases the impedance (resistance) of the metal surface which in turn decreases C_{dl} values.

SEM Studies

SEM photographs of polished mild steel surface on blank 1N H_2SO_4 and in H_2SO_4 and with AF leave extract are shown in photograph 1 and 2. The morphology shows a characteristic uniform corrosion of mild steel in blank acid whereas with inhibitor a smooth surface is visible.



**Figure 6: Mild Steel Specimen Immersed
in Blank 1N H_2SO_4**



**Figure 7: Mild Steel Specimen Immersed in 1N H_2SO_4
with Blank 1N H_2SO_4 0.6 v/v AF Extract**

Mechanism

Phytoconstituents of *Acalypha fruticosa*

Acalypha fruticosa contains triter penoids, steroids, saponins, tannins, phenols, flavonoids, alkaloids, anthraquinones and sugars. 1, 2- Benzenedicarboxylic acid diisooctyl ester, n-Hexadecanoic acid, 9, 12-octadecadienoic acid [z, z], $\hat{I}\pm$ -D-glucopyranoside and eicosyltrichlorosilane^[16] and flavanoids as the major constituent and these may get adsorbed on the metal surface and this adsorption on the mild steel might probably bring about the inhibition of mild steel dissolution.

CONCLUSIONS

The AF leaf extract acts as good corrosion inhibitor for mild steel. Inhibitor efficiency of 97.92% is obtained for 0.3% v/v inhibitor concentration. Potentiodynamic studies indicate that the inhibitor exhibits mixed mode type action inhibition both anodic and cathodic process. Corrosion rate decreased considerable with increase in concentration of inhibitor for all temperatures studied showing that inhibition of corrosion takes place by adsorption process.

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